



Voltammetry of MicroParticles in Thin Layer



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ABSTRACT

We describe a new experimental device for the characterization of electroactive microparticles and of the soluble species released during their electrochemical transformation. By using only a few microparticles, it provides, in a faster way, similar information as modified carbon paste electrodes with electrolytic binders (CPEEBs) and the sensitivity and resolution are much better. The device geometry was modelled with ferrocyanide ions and the voltammograms for ferrocene, pyrolusite and hematite were compared with the literature ones concerning CPEEBs. Finally, an alumina-supported palladium catalyst and pyrite-containing argillite were successfully characterized.

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1. Introduction

Voltammetry of microparticles (VMP) is a technique developed by Scholz [1] that can be applied for the voltammetric characterization of any solid electroactive material, conducting or not, via the mechanical immobilization of microparticles on the cross section of a current collector [2–5]. This latter is most often a graphite rod which had been previously impregnated with solid paraffin to fill up the graphite pores. VMP has the advantages over carbon paste electroactive electrodes of requiring only a few micrograms of matter to be analyzed and avoiding the use of organic binders that can influence the electrochemical behaviour of the solid compounds. However, VMP cannot provide information on the soluble species released in solution by the immobilized microparticles during their electrochemical transformation. When the electrochemical kinetics is slow and voltammetry at rapid scan rates is inoperable. To get this information today, electrochemists can utilize Carbon Paste Electrodes with Electrolytic Binders (CPEEBs), which have been developed in the seventies by the Bauer group who established a theoretical model on their working principle [6–8]. CPEEBs are prepared by mixing graphite powder with electrolytic solutions instead of non-conducting pasting liquids with traditional modified carbon paste electrodes [9]. In this way, in principle, the whole of the electroactive matter inserted in the carbon paste is electrochemically transformed and soluble species

released are trapped in the carbon paste. These electrodes have been successfully used with various compounds just as well insoluble (ferrocene [6], uranium ores [10], copper sulphides [11–14], ilmenites [15], oxides of iron [16–21], copper [21] and manganese [22]) as dissolved directly in the electrolyte (FeCl_2 and MnCl_2 [22], $\text{Fe}(\text{CN})_6^{4-}$ and O_2 [6]). Ramirez et al. proposed some experimental modifications [23] and the Vittori group introduced theoretical complements on the Bauer model [24,25]. Nevertheless, when CPEEBs are employed, extremely slow scan rates (in the range of some hundredths or tenths of mV/s) and very concentrated supporting electrolytes are used in order to minimize capacitive currents. Moreover, the effective deaeration of the carbon paste is quite hard (use of vacuum and glove boxes or previous electrochemical reduction of atmospheric oxygen if possible). In addition, if the solubilization of the non-conducting electroactive microparticles is very slow, the faradaic current becomes of the same order of magnitude as the background current [6].

We developed an experimental device that comes from the combination of VMP and thin-layer (TL) voltammetry [26] that we called ‘Voltammetry of MicroParticles in Thin Layer’ (VMPTL) [27]. Its principle consists in entrapping a very small amount of electroactive material (some micrometric or submicrometric particles) and a TL of electrolyte solution between the cross sections of two graphite electrodes. VMPTL provides similar information as CPEEBs while maintaining the benefits of VMP. In this way, the voltammetric characterization of both the entrapped microparticles and the soluble species released by the latter can be performed with a much higher sensitivity and resolution than CPEEBs with only a few micrograms of matter. In addition, the

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solution can be easily deaerated before the entrapping stage by bubbling an inert gas and ten times faster scan rates can be used.

The aim of this paper is to show the potentiality and performance of VMPTL in comparison with CPEEBs. After the description of the experimental device, its functioning will be tested with the model electrochemical system $\text{Fe}(\text{CN})_6^{3-/4-}$. Then, the voltammograms recorded for ferrocene (Fc), pyrolusite (MnO_2) and hematite (Fe_2O_3) will be compared with the literature ones obtained with CPEEBs. Finally, VMPTL will be utilised for the characterization of two electroactive compounds that are at percent levels in more or less complex matrixes: metallic palladium in an alumina-supported catalyst and pyrite (FeS_2) in Callovo-Oxfordian argillite. The present approach could be also useful for studies of organic deposits, as it has been pioneered by Doménech-Carbó [28,29].

2. Experimental

2.1. The electrochemical cell

Experimental setup: some electroactive microparticles and a TL of solution are entrapped between the cross sections of two graphite rods. The rods are mounted, with an epoxy resin (Epofix kit from Struers), in the axis of the truncated plungers of two glass syringes that allow to the rods to slide hermetically inside the end truncated syringe barrels (Fig. 1A). The rods are externally short-circuited and connected to the working electrode input of the potentiostat.

The main purpose of using two short-circuited graphite electrodes opposite each other instead of only one against an insulating surface, as with classic thin layer cells, is to ensure a good electrical contact with the immobilized electroactive microparticles allowing the electrochemical transformation of the greatest possible number, if not all, of them.

Before mounting the graphite rods (3.05 mm diameter, 99.9995% metals basis from Alfa Aesar) in the truncated plungers of the syringes it is necessary to fill up the graphite pores with solid paraffin to eliminate the electrochemical response of adsorbed oxygen and to avoid the contamination of graphite by soluble species as recommended by Scholz [1].

Cell design: the cell, depicted schematically in Fig. 1B, is made of Perspex and has a cylindrical shape. There is a central cylindrical conduit, containing the electrolytic medium, where are stuck horizontally with a bicomponent epoxy glue the syringe barrels where the two graphite electrodes are allowed to move. A platinum counter electrode inserted in a PTFE stopper is screwed on the basis of the cell and, according to the experiment, a silver-wire used as the quasi-reference electrode or a Ag/AgCl reference electrode are inserted in a PTFE stopper on the top of the cell. An inert gas inlet tube is also inserted in the top stopper. Depending on the position of the tube, the gas is bubbling through the solution or it maintains an inert atmosphere over its surface. The device is equipped with a metallic holder and a slight rotation about its axis allows to remove one after the other the graphite electrodes for cleaning or polishing without emptying the cell.

2.2. Use of the device

To transfer and immobilize the electroactive particles inside the TL, a few grains are applied to the graphite surface of one of the electrodes and pressed on it with a small spatula. Then the electrode is softly struck against a glass surface before its introduction in the electrochemical cell in order to remove the particles that were badly fixed. After deaeration of the solution, the graphite electrodes are pushed up and rotated one against the other in such a way that the immobilized microparticles come in the most intimate contact with the two graphite discs. Before each experiment the surface of the electrodes is cleaned by polishing with a filter paper or with a grinding paper, if necessary.

2.3. Electrochemical measurements

Voltammetric experiments were performed with a model 174A polarographic analyzer (EG&G-PAR), which was interfaced via a computer AD card and monitored by a home-made application created by means of the TestPoint™ software, or with a 'Quadstat' four-channel potentiostat used as a single three-electrode potentiostat and monitored by the EChem Software (both from EDaq). According to the experiments, the potentials were referred to the silver quasi-reference electrode (Ag/QREF) or to the saturated Ag/AgCl electrode.

2.4. Chemicals and minerals

Potassium hexacyanoferrate(II), sulphuric and hydrochloric acids and potassium chloride, were of RP Normapur grade from Prolabo. Ferrocene purum grade, manganese(IV) oxide puriss. grade and iron(III) oxide puriss. p.a. grade were obtained from Fluka, and palladium(II) chloride from Merck. Palladium on alumina pellets loading 5 wt. % catalyst was from Johnson Matthey (see SECM characterization in Fig. 2A). The Callovo-Oxfordian argillite sample containing 0.5–1 wt. % pyrite [30] came from Bure (Meuse) in France (optical microscope picture in Fig. 2B). It was

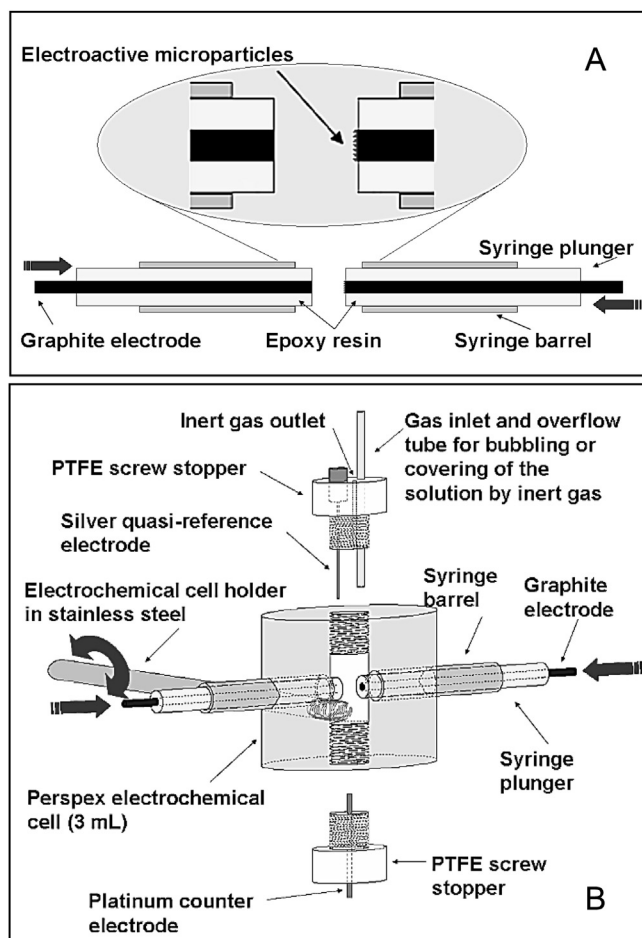


Fig. 1. The VMPTL electrochemical cell: (A) experimental setup, (B) schematic representation of the cell design.

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